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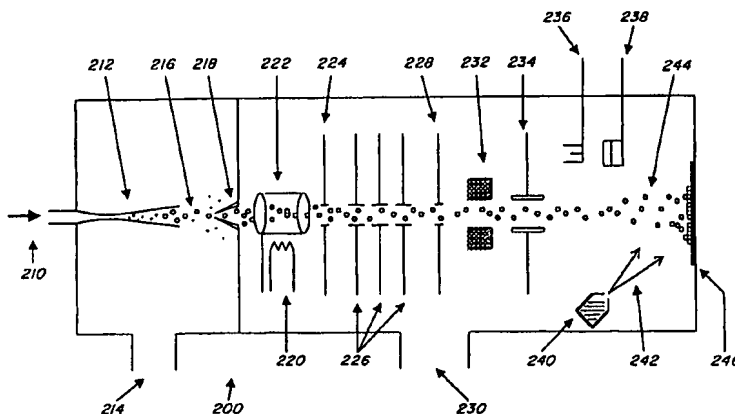
(57) Abstract

A method and apparatus for formation of very thin nitride onto the surface of a monocrystalline substrate wafer. Such nitride films include silicon nitride on silicon wafers, and gallium nitride and its alloys on gallium arsenide, sapphire and SiC wafers. These films are formed with lower processing temperatures, are of excellent dielectric quality, and suitable for use in semiconductor devices. The thin nitride films are produced by surface bombardment with a beam of gas–cluster ions at low energy per atom within clusters of typically a few thousand atoms. The gas can be any condensable gas containing nitrogen, such as N_2, NO, N_2O, NH_3, or any such mixed with another condensable gas, such as H, He, Ar or O_2. Films are formed as a result of chemical reaction of the nitrogen–containing beam with the substrate, or by additional employment of various sources, such as silicon, gallium or aluminum from a physical vapor source, or by including a silicon–containing gas mixed with the nitrogen–containing gas in the cluster ion beam. The nitride films may be used as dielectrics or semiconductor layers in microelectronic and photonic devices.

GAS CLUSTER ION BEAMS FOR FORMATION OF NITRIDE FILMS

PRIORITY INFORMATION

This application claims priority from provisional application Ser. No. 60/106,859

5   filed November 3, 1998.

BACKGROUND OF THE INVENTION

The invention relates to gas cluster ion beams for the formation of nitride films.

The heart of high-density memory and microprocessor chips is a very thin film of

10   an electrically insulating material formed on the surface of a silicon crystal wafer. This

insulator, referred to as the gate dielectric, must sustain very high electric fields and serve

efficiently as the key component in the storage of electrical charge. A conductor film, not

necessarily a true metal, must then be formed on top of the dielectric.

Two basic types of microelectronic devices are fabricated from these so-called

15   metal/insulator/silicon (MIS) layered structures, namely bit storage or "memory", and

logic transistors. An assembly of many bit-storage units on a single silicon wafer is used

to fabricate dynamic random-access memory (DRAM) integrated circuits, while an

assembly of many logic transistors is used to fabricate microprocessors. As the chip

industry moves toward smaller circuit elements packed more tightly on the chip, it is

20   required that the area devoted to each charge-storage circuit on the chip be smaller but

store at least the same amount of charge.

Two approaches are possible, first the thickness of the gate dielectric film can be

reduced and second the intrinsic storage ability of that insulator, called its dielectric

constant, can be increased by choice of a new kind of material. Up until the present time,

25   the chip industry has used silicon oxide (nominally SiO_2, often referred to as just "oxide")

as the dielectric and has succeeded in making each chip generation with thinner oxide

films. When the insulator is this oxide, then the structures consisting of a conductor

(metal or polysilicon) film, on an oxide film, in turn on silicon is the metal/oxide/silicon

(MOS) structure employed as the basic building block unit of the vast majority of the

30   semiconductor industry product. However, the trend of continuing to reduce the thickness

of the oxide in the MOS is projected to run out of potential as it reaches basic physical

limits.

Research into new materials has found that a compound known as silicon nitride

(nominally Si_3N_4) may satisfy industrial requirements, at least for a few years, for a gate dielectric film with a higher dielectric constant. The dielectric constant (κ) for Si_3N_4 is about 4.2 compared with about 2.13 for SiO_2, at low frequencies. Considerable effort has already been expended on developing apparatus and methods to fabricate thin silicon

5　　nitride films. It has so far been unavoidable not to have the quality of this material compromised by either poor atomic structure, unsatisfactory stoichiometry (ratio of number of silicon atoms to those of nitrogen), or unwanted impurities such as oxygen or hydrogen.

　　　　　For example, if the silicon nitride films are formed with a few silicon or nitrogen

10　　atoms having defective or missing bonds, then these can attract and hold (trap) temporarily some of the electric charge, binding it too tightly for efficient use by a DRAM or microprocessor chip circuit. Traps can form deep in the film or at a subsurface interface. The interface between the dielectric film and the silicon may have various types of defects most of which will limit the performance of an MIS device constructed from that film.

15　　It is found generally, that such interfacial defects are the most difficult to minimize sufficiently such that high-performance MIS devices can be fabricated. The interface between SiO_2 and silicon is presently of the highest quality and of the lowest areal density of all defects known for any dielectric film on a semiconductor, including those with larger dielectric constant such as Si_3N_4. All of these types of defective films are caused

20　　by limitations inherent in the apparatus, method and source materials used to fabricate the films as well as factors intrinsic to the differing materials properties of the film and the silicon.

　　　　　The greatest differences intrinsic to Si_3N_4 films and Si wafers are: (1) the structural mismatch occurring for an amorphous or microcrystalline material, the Si_3N_4, and a

25　　monocrystal of different composition, the Si, (2) the differing thermal coefficient of expansion (TCE), and (3) the stress within the Si_3N_4 film. It is a practiced method that silicon nitride films may be fabricated with a somewhat higher stoichiometry ratio Si:N, i.e., silicon rich, than that of the base composition 3:4, with the result that the film stress after deposition onto silicon is greatly relaxed. Such off-stoichiometry films however may

30　　be more prone to charge trapping (electronic defects) that occur as a consequence of bonding (structural) defects. It is known in the art to provide at least partial passivation of such bond defects by providing hydrogen or oxygen, such as during a thermal anneal, which can bond at each defect site in the film.

Passivation with hydrogen or oxygen also induces defects, such as nonbonding electron orbitals on each oxygen atom that become immobile states within the band gap of the dielectric film. Another defect type are the highly localized stress centers within the film as a result of inserting the hydrogen or oxygen atoms into a space that otherwise

5   would have held a silicon or nitrogen atom, or inserted interstitially within the silicon nitride bonded structure. It is important to note that without very good vacuum practice, the physical vapor deposition (PVD) apparatus and silicon nitride film source materials may inadvertently introduce oxygen or hydrogen into the film during deposition. This can occur if the background pressure of residual water vapor in the PVD system is not low

10 enough to avoid physisorption of the water vapor followed by chemical activation and bonding due to the film deposition activity. In addition, the source materials may be impure or contain oxygen or hydrogen for convenience, as is the case with nitrogen sources that consist of some form of ammonia.

Bonding and electronic defects in dielectric thin films can be at least partially

15 avoided by performing the deposition at an elevated temperature or by following the deposition by annealing at an elevated temperature. Film defects will tend to be healed by the application of either of these in-situ or post-deposition annealing processes, since at higher temperatures there is increased mobility of the atoms within the film. Many types of defects cause configurations of the atoms that increase the thermodynamic free

20 energy above that of the defect-free material, and hence the higher mobility during an anneal allows the film to reconfigure into a lower energy and lower defect density state. Either of these methods of fabrication and annealing of thin films will cause stress between the film and substrate (silicon) due to any differential TCE, as there is between Si_3N_4 and Si. Lower annealing process temperatures, i.e., temperatures closer to typical

25 ambient temperatures of 25°C, will reduce any defects induced by mismatched TCE. Hence, it is preferred in selecting film deposition methods to reduce process temperatures whenever possible.

Thermal nitridation of silicon surfaces is standard industry practice whereby silicon is heated to 950 - 1200°C in a furnace and exposed to ammonia gas. The silicon nitride

30 film that forms is self-limiting in thickness due to the diffusion-limited growth, as are most native films. The growth curves describing film thickness increase roughly as saturating exponential functions, requiring, for example about 4 hours of process exposure to form a 55 Å thick film. Nitrogen gas in a furnace requires an impracticably long time to form

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a native silicon nitride film on silicon, since the cracking energy for N_2 is much higher than it is for NH_3. Similar results are experienced for silicon oxynitride films (SiO_xN_y) formed from SiO_2 films in hot ammonia vapor. Molecular beam epitaxy (MBE) methods have been reported utilizing ammonia gas or nitrogen gas directed onto hot silicon

5   surfaces, in high vacuum, to form silicon nitride and closely related silicon oxynitride compounds. Other reported MBE methods use nitrogen ion irradiation of a silicon surface to reactively form silicon nitride.

Nitride semiconductors of the groups III-V, such as GaN, AlN, InN and their alloys, offer high bandgap energies, excellent electrical, thermal and physical properties,

10   and other important characteristics. Growth of semiconducting nitride materials has been an area of active interest for more than a decade. Nitride semiconductors are expected to have widespread applications in future electronic and optoelectronic devices, but in order for these applications to be realized, very substantial advances are still required in techniques for depositing high quality nitride semiconductor materials upon appropriate

15   substrates such as SiC or sapphire. Among many issues that must be addressed are included high defect densities, film inhomogeneities, poor surface morphologies, and large stress effects associated with high growth temperatures and thermal expansion mismatch with substrates. In physical vapor deposition (PVD), the group III material is relatively easy to provide by way of a metal (Ga, Al and In) evaporation or sublimation source.

20   However, the nitrogen source is a principal limitation of all present PVD methods.

A number of growth techniques for GaN films have been reported including various low-pressure and plasma-enhanced metalorganic chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) processes such as the reactive-ion MBE or gas-source MBE. Those methods that utilize a nitrogen source consisting of a compound of nitrogen

25   other than N_2, such as ammonia gas (NH_3) limit the quality of the formed GaN films due to incorporation of some of the hydrogen within the films. In order that semiconductor devices can be fabricated from the intrinsic GaN materials (e.g., GaN, AlGaN, InGaN or AlInGaN) the nearly pure form must be doped with other elements. Many elements have been used for this purpose and good quality n-type materials are fabricated. The presence

30   of small amounts of incorporated hydrogen in p-type GaN limits the activation of (passivate) acceptors in this material. MBE sources of nitrogen that utilize an rf-plasma or electron cyclotron resonance to excite N_2 and thereby increase its reactivity for film formation, all suffer from unintended contamination of the films due to plasma sputtering

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of the vacuum chamber walls which cause impurities to be introduced into the film.

Thus, new methods of fabricating silicon nitride films on silicon and III-V nitride films are needed. New silicon nitride methods will make it possible for the chip industry to substantially shrink the size of each microcircuit element and thus pack them to greater density providing the chip with more power in future generations of these silicon chips. Further, improved methods of fabricating gallium nitride materials will enable improved microelectronic and photonic devices. Such devices including blue and ultraviolet light emitting diodes (LED) and lasers, high-voltage and high-temperature transistors with considerable tolerance for exposure to ionizing radiation.

Highly enhanced chemical-reaction characteristics are experimentally observed in gas-cluster ion-beam (GCIB) processes and are attributed to the low velocity of the clusters, the low energy per incident atom, and the induced transient of extreme temperature and pressure which are produced upon impact of the clusters. The collision of nitrogen-clusters with a surface causes the diatomic nitrogen molecules to crack, and there is a brief time during which the nitrogen is available to react with that surface. As one example, it has been demonstrated that if O_2 or CO_2 are used as GCIB source gases for cluster bombardment of Si, then an SiO_2 layer of controllable thickness up to a maximum of approximately 120 Å, depending upon cluster ion dose and energy, can be formed at room temperature. MOS capacitors fabricated using these oxide layers have exhibited excellent current-voltage and capacitance-voltage characteristics.

As additional examples, GCIB-assisted reactive film deposition has been demonstrated for fabrication of lead oxide (PbO) and indium-tin oxide (ITO) films. Characterizations of these films have shown excellent stoichiometry of the deposited materials, most notably with respect to oxygen content. Because of the mixed valence possible with inorganic compounds of metals and low energy of oxygen vacancies, metal-oxide compounds are often difficult to prepare with full oxygen content. ITO films are important for use as optically-transparent and electrically-conducting electrode layers in semiconductor emitters and flat-panel displays. Even a small oxygen substoichiometry in ITO leads to a considerable reduction in the conductivity of the films and thus limits their performance. ITO films are typically deposited onto hot substrates, which makes use of certain types of substrates, such as plastics or polymers, impractical. Low-temperature oxygen-GCIB-assisted processes for ITO films are presently being developed for use in flat panel displays on plastic substrates.

SUMMARY OF THE INVENTION

Accordingly, the invention provides a method and apparatus for formation of very thin nitride films onto the surface of a monocrystalline substrate wafer. Such nitride films include silicon nitride on silicon wafers, and gallium nitride and its alloys on gallium

5   arsenide, sapphire and SiC wafers. These films are formed with lower processing temperatures, are of excellent dielectric quality, and suitable for use in semiconductor devices. The thin nitride films are produced by surface bombardment with a beam of gas-cluster ions at low energy per atom within clusters of typically a few thousand atoms. The gas can be any condensable gas containing nitrogen, such as N_2, NO, N_2O, NH_3, or any

10   such mixed with another condensable gas, such as H, He, Ar or O_2. Films are formed as a result of chemical reaction of the nitrogen-containing beam with the substrate, or by additional employment of various sources, such as silicon, gallium or aluminum from a physical vapor source, or by including a silicon-containing gas mixed with the nitrogen-containing gas in the cluster ion beam. The nitride films may be used as dielectrics or

15   semiconductor layers in microelectronic and photonic devices.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a table providing a brief description of the advantages and disadvantages

20   of conventional nitride growth processes and comparisons with the potential for the GCIB approach of the invention;

FIG. 2 is a functional block diagram of an accelerator apparatus in accordance with the invention;

FIGs. 3A and 3B are graphs of the XPS of a sample that was exposed to a nitrogen

25   cluster beam onto an unheated native oxide surface of silicon;

FIGs. 4A and 4B are graphs of the XPS of a sample that was exposed to a nitrogen cluster beam onto an unheated HF-etched surface of silicon;

FIGs. 5A-5C are graphs of the XPS of a sample described herein as deposition of Ga and N that was exposed to nitrogen cluster and gallium beams onto an unheated HF-

30   etched surface of silicon; and

FIGs. 6A-6C are graphs of the XPS of a sample described herein as deposition of Ga and N that was exposed to nitrogen cluster and gallium beams onto the surface of sapphire at about 750°C.

DETAILED DESCRIPTION OF THE INVENTION

The field of applications for the methods of the invention as to gas-cluster ion beam (GCIB) nitride film formation, include the use of argon-GCIB for *in-situ* cleaning and micro-smoothing of interfaces by removal of a few atomic layers, done in preparation

5   for deposition of nitride dielectric or epitaxial layers; direct formation of Si_3N_4 dielectric layers less than 100 Å thick by reactive bombardment by nitrogen-gas-cluster ions of a silicon-wafer surface at low temperatures; direct formation of AlN thin films by reactive bombardment by nitrogen-gas-cluster ions of a sapphire-wafer surface at low temperatures; direct formation of GaN thin films under reactive bombardment by nitrogen-gas-cluster

10   ions of a GaAs-wafer surface at low temperatures; deposition of Si_3N_4 dielectric thin films by reactive bombardment by nitrogen-gas-cluster ions of a substrate surface at relatively low temperatures and under concurrent vapor flux of a silicon source; and deposition of AlN, GaN or TiN thin films by reactive bombardment by nitrogen-gas-cluster ions of a substrate surface at relatively low temperatures and under concurrent vapor flux of an

15   aluminum, gallium, or titanium source.

Alternatives for formation of nitride-compound thin films with PVD methods are various high-vacuum based techniques that employ nitrogen as a diatomic gas, as a gas of radicals and excited states, as a beam of ions, and as a cluster-ion beam. Such techniques include rf-plasma nitrogen, electron-cyclotron resonance (ECR) nitrogen, ammonia gas-

20   source MBE. The table of FIG. 1 provides a brief description of the advantages and disadvantages of these leading nitride growth processes and compares them with the potential for the GCIB approach of the invention.

One process effect associated with gas cluster ion impact involves exceptionally enhanced chemical reactivity between gas atoms of the cluster and atoms of the target

25   surface. This effect is of importance for practical growth of nitride semiconductor thin films at low temperatures. Because the energies of individual atoms within a cluster ion are very small, typically a few eV or less, the atoms penetrate through only a few monolayers of the target surface during impact. All of the energy carried by the entire cluster ion is consequently deposited into an extremely thin volume at the impact site

30   during a period of about 10^{-12} second.

Because of the high total energy of the cluster ion and extremely small interaction volume, the deposited energy density at the impact site is far greater than in the case of bombardment by conventional ions and the resulting thermal-spike conditions are greatly

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enhanced. Computer simulations have suggested instantaneous temperatures of the order

of 10^5 K together with mega-bar instantaneous pressures at cluster ion impact sites. The

extreme instantaneous temperature and pressure conditions, in combination with intimate

mixing between gas atoms from the cluster ion and the target material atoms, is considered

5   to be responsible for highly enhanced ambient temperature reaction effects that have been

observed. The reports of enhanced reaction involved oxidation effects produced by O_2 and

CO_2 cluster ions.

Conventional monomer and small-mass ion plasmas and ion beams cause

considerable damage to very smooth thin-film surfaces and to the region just below the

10   surface. By reducing the ion energy, the damage can be reduced, but the effects of the

process are also reduced. Thus, the monomer sputter etch rate declines as the ion energy

is reduced and hence a higher dose of low-energy ions are required to obtain the same etch

depth. As a consequence, this method becomes impractical at energy low enough that it

causes very little damage. Gas-cluster ion-beam processes on the other hand do not suffer

15   these limitations and high-yield sputtering with argon clusters is possible at low energy.

Likewise, nitrogen-gas clusters have high rates of reactivity combined with low rates of

introducing damage into the substrate and formed thin film that will provide industry with

a substantial advantage over conventional ion processes.

According to the invention, a beam of ion-clusters is formed from gasses with

20   nitrogen, including N_2, N_2 mixed with Ar, N_2O, NO, and NH_3. In an exemplary

embodiment, substrate surfaces are readied for nitride-film formation by first utilizing Ar-

cluster beam bombardment to decontaminate, etch and smooth the substrate surfaces. This

also serves to increase the availability of high-energy surface bonds thereby increasing the

probability of nitrogen bonding and film formation. According to the invention, the

25   surface undergoing argon-cluster cleaning is immediately bombarded by the nitrogen-

cluster beam in such a manner that the very clean high-energy surface is not allowed any

appreciable time or atmospheric exposure during which it will be contaminated prior to

formation of the nitride film. According to the art of surface preparation with exposure

to an argon-gas cluster ion beam, superior decontamination, and very low damage are,

30   possible. The invention improves on this process by providing for film deposition without

loss of this superior surface preparation.

In another exemplary embodiment, the formation of clusters consisting only

partially of nitrogen are formed of an argon cluster-ion beam mixed with a fraction of

nitrogen gas. For nitrogen content less than about 20%, the N_2 dissolves into the Ar

clusters, and the clusters are essentially a binary liquid mixture. The impact of such

clusters will utilize the mass of argon in the cluster to promote cracking of the diatomic

nitrogen, and hence the advantage of the method for formation of nitride films. Higher

5   concentrations of N_2 are expected to phase separate from the Ar, forming into clusters of

two types: those of mainly N_2 and those of mainly Ar.

In another exemplary embodiment, nitrogen clusters are formed from a mixture of

N_2 and helium source gases. The latter does not condense and form clusters itself, if the

supply gases are kept at near room temperature. About 30% helium content is estimated

10   to be optimal. The He assists in removing heat from the N_2 gas as it transits the nozzle,

thus cooling the N_2 gas, and thereby improving the efficiency of the cluster formation

process.

Ammonia gas can be condensed into clusters and reactively form nitride films.

Also, ammonia is known as a molecular (but not a cluster) source of nitrogen in MBE

15   growth of Si_3N_4, GaN and related films. Using ammonia carries serious the complications

of both safety and greater impurity content, and hence a higher cost for purified gas. In

addition, ammonia in gas-source MBE has a low efficiency of reactive formation of GaN

films, so that large quantities of high-purity ammonia must be used.

Experimental realization of nitrogen-gas clusters formed into an ion beam and used

20   to cause reactive nitridation of a silicon wafer surface as well as realization of GaN film

deposition on sapphire by this ion beam in the presence of a gallium thermal flux is

provided by the invention. FIG. 2 is a functional block diagram of an accelerator

apparatus 200 in accordance with the invention utilized for these experiments. A

hypersonic jet of nitrogen gas is formed by a high-pressure nitrogen gas 210 expanding

25   through a Laval nozzle 212 into a first vacuum chamber 214. When the nozzle dimensions

are chosen correctly, nominally a bore diameter of 0.1 mm and length of 25 mm, and

sufficient pressure (about 10 atmospheres) is used to force the nitrogen gas through the

nozzle, then sufficient Joule-Thompson cooling of the gas occurs and very small droplets

or clusters 216 form. These clusters have a wide distribution in sizes, from roughly 500

30   to 5000 N_2 molecules contained in each cluster. The first vacuum chamber 214 is

maintained at about 10^{-2} Torr by means of a vacuum pump. This neutral jet of nitrogen-

gas clusters enters a second vacuum chamber by way of a pin hole orifice or skimmer 218

in the form of a cone that points upstream. This configuration serves to "skim" the gas

jet and thereby allow only the core of the jet to pass into a second vacuum chamber 230. Most of the clusters are found in the core of the jet and pass through the skimmer while residual, unclustered gas is rejected.

Better selection occurs if the skimmer is further downstream from the nozzle,
5   however, a Mach disk forms due to the supersonic velocity of the jet and the skimmer must be at least slightly upstream of that location. In this system with the nozzle and gas pressures in use, the optimum skimmer location was 2 or 3 cm from the exit flange of the nozzle. A large pumping differential is sustained across the skimmer and the second chamber 230 is typically at about $5x10^{-6}$ Torr when the beam is present.

10   The jet of clusters that exits the skimmer 218 and enters the second chamber passes into the axis of a cylindrical wire mesh 222. A hot tungsten filament 220 near, but outside of that mesh creates a flux of energetic electrons that impact the jet of clusters and ionizes them (positive) as they pass along the core of the cylindrical mesh. The wire mesh is biased to about 100 V positive and this serves to set the electron impact energy. The
15   clusters become singly ionized in this process and hence the cluster ions have a very small charge-to-mass ratio. These ions are extracted from the ionized region by potential plate 224, e.g., 2 kV, whereupon they enter a three-element Einzel lens 226 for beam focusing and then to a final plate 228 at high attractive potential for beam acceleration.

All of the plates are disk shaped with a central round opening (about 5mm in
20   diameter) for the beam to pass through. Since the final disposition of the beam is to strike a substrate in the process chamber, it is most convenient if that sample is at the ground potential of the process chamber. For this reason, the accelerator is configured so that the positive ions are accelerated toward ground from the upstream region where the ions are formed within the cylindrical wire mesh which then must be at the highest positive
25   potential. Typical accelerating potentials that function well in this system are 10 to 30 kV. For such acceleration potentials, clusters composed of 1,000 or 3,000 molecules, respectively, will have only about 10 eV of average energy per molecule, which is extremely low relative to other types of ion beams.

Soon after the final plate 228 in the accelerator stack, the beam enters a region of
30   the second vacuum chamber 230 where beam diagnostics are done. Either a neutral-gas pressure gage 236 or a small Faraday cup 238 can be inserted into the beam to measure either the quantity of gas in the beam or the ion current in the beam. These monitors are used as diagnostics during the system tuning phase.

Before the cluster beam strikes the target or substrate, all of the small-mass ions, typically these are almost exclusively monomers, are filtered out by a magnetic-field sector 232. This magnetic field is transverse to the beam propagation axis, and thereby acts to divert out of the beam any monomers and small mass species that are present. For the

5   nitrogen beam of this system, a field of the order of 1 or 2 kG serves well to filter the cluster beam. Essentially, this filter serves as a "high pass" filter for all large-mass ions.

A characteristic of the cluster nucleation mechanism is that the thermodynamic stability of very small clusters is not favorable, so only monomers and relatively large clusters survive in any number after the few microseconds that are required for propagation of the

10   beam from the nozzle to the target.

Two pairs of parallel plates 234 serve to deflect the ion beam by way of electric fields perpendicular to the beam and created by a differential voltage between the plates in each pair. The beam deflection plates are driven by time varying voltages in such a manner as to electrostatically scan the ion beam 244 over the full area desired of a work

15   piece surface 246.

For deposition of gallium-containing films, an effusion cell 240 serves as a sublimation source of gallium vapor 242 that falls on the substrate in the final vacuum chamber coincident with the nitrogen-cluster ion beam. The gallium effusion and deposition rate was calibrated by use of a quartz crystal microbalance.

20   Substrates that are to have GaN deposited are mounted onto a small, flat-plate heater 246 consisting of a carbide disk covered with boron nitride. This heater was calibrated by mounting a clean silicon wafer chip and observing its IR emission with a pyrometer through a viewport in the vacuum chamber. Typical substrate temperatures during deposition are in the 600°C to 800°C range.

25   To characterize the presence of nitrogen clusters in the ion beam, a test was performed. It is known that an actual cluster beam will smooth the surface of a gold film. The gold will not react with the beam or the chamber ambient, and any appreciable monomer content in the beam will tend to roughen the surface (a well-known property of conventional high-energy ion beams). Gold films exposed in this apparatus to the

30   nitrogen-cluster ion beam were found to have the surface roughness reduced when evaluated by an atomic force microscope.

In subsequent experiments, the nitrogen-cluster ion beam was used to bombard the surface of silicon wafers. Two types of nitrogen-cluster beam experiments were carried

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out to explore the possibility of surface reactions and nitride-compound formation with those surfaces, i.e., nitridation reactions. Silicon wafers were chosen because of the wide extent of knowledge of these surfaces and their easy availability. Both silicon with its native oxide and silicon that had been processed with aqueous solutions of HF, which

5   serves to remove that oxide, were utilized.

Exemplary experimental processing in accordance with the invention is now described.

Initially, nitridation of native silicon surfaces will be described. A 1-cm square chip of a commercial silicon wafer was degreased and mounted into the deposition chamber. As

10   such, this wafer sample had a "native" oxide (SiO_2) film on the surface, typically about 2 or 3 nm thick. The unheated samples were bombarded in vacuum with a nitrogen-GCIB formed from pure (molecular) nitrogen gas, ionized, accelerated through 15 kV, and impacted at normal incidence onto the sample substrate. Typical beam quality limited the beam current to about 90 nA falling onto the sample.

15   Nitridation of hydrogen-terminated silicon surfaces will now described. A 1-cm square chip of a commercial silicon wafer was degreased, dipped into 3% HF solution, blown dry and mounted into the deposition chamber. The HF process etches only the (native) oxide film, stopping abruptly at the silicon interface, and leaving behind a weakly-bound single atom thick (monolayer) of hydrogen atoms on the silicon. The hydrogen is

20   removed by heating in vacuum to above 400°C or by a substitutional process under bombardment with a reactant such as the nitrogen clusters. These unheated samples were bombarded in vacuum with a nitrogen-GCIB formed from pure (molecular) nitrogen gas, ionized, accelerated through 15 kV, and impacted at normal incidence onto the sample substrate. Typical beam current was ~110 nA onto the sample itself.

25   Gallium nitride films were then formed on two substrates. The depositions were as follows. Deposition of Ga and N onto a hydrogen-terminated silicon surface is now described. A 1-cm square chip of a commercial silicon wafer was degreased, dipped into 3% HF solution, blown dry and mounted into the deposition chamber. The unheated samples were bombarded in vacuum with a nitrogen-GCIB formed from pure (molecular)

30   nitrogen gas, ionized, accelerated through 15 kV, and impacted at normal incidence onto the sample substrate. Typical beam current was ~110 nA onto the sample itself. After the beam was established upon the surface, the gallium source was heated and held for 20

min at 950°C, then cooled rapidly and the beam halted.

Deposition of Ga and N onto a sapphire surface will now be described. A 1-inch round commercial sapphire wafer was degreased, blown dry and mounted into the deposition chamber. The sample was heated to about 750°C and then bombarded with a nitrogen-GCIB formed from pure (molecular) nitrogen gas, ionized, accelerated through 15 kV, and impacted at normal incidence onto the sample substrate. Typical beam current was ~100 nA onto the sample itself. After the beam was established upon the surface, the gallium source was heated and held for 50 min at 950°C, then cooled rapidly. Thereafter, the beam was halted and the sample cooled.

In these experiments, the nitrogen beam current was 100 nA total, falling onto the square of the target sample, 1x1 cm^2. This is about 6 x 10^{11} ions/sec or 2.5 x 10^{15} atoms/s (nominal average cluster is 2000 diatomic molecules of nitrogen). A nominal surface density of a solid target is about 7 x 10^{14} atoms/cm^2, that of Si(100), defined here as one monolayer. Thus, the beam delivers roughly 4 monolayer/sec to the sample. If 100% of the nitrogen in the cluster beam is incorporated into a growing GaN film, the growth rate would be as high as roughly 7 Å/s or 2 µm/hr. Formation of very thin films requires limiting the incorporation rate of background gas species such as oxygen. The base pressure of the deposition chamber is preferably well below roughly 10^{-8} Torr.

The four samples described above were analyzed with x-ray photoemission spectroscopy (XPS or ESCA). The major electron emission peaks observed from these samples are shown in the graphs of FIGs. 3-6. With each electron spectral line are the approximate assignments of the chemical bonds that are the source of emission at that binding energy.

FIGs. 3A and 3B are graphs of the XPS of a sample that was exposed to a nitrogen cluster beam onto an unheated native oxide surface of silicon. In FIG. 3A, the graph shows the *2p* electrons from silicon in the sample described herein as the nitridation of native silicon surfaces. At ~99-100 eV, the small curve is the emission from Si-Si bonds, at ~101-102 eV is Si-N, at ~103 eV are the suboxide SiO$_x$ (x<2), and with the highest binding energy (bonds with the most electron transfer away from the silicon atom) at ~104 eV is SiO$_2$. The oxides SiO$_2$ and SiO$_x$ are the native oxide, as expected, but clearly some of the native oxide has been substituted with nitrogen to form a silicon nitride compound. In fact, the most likely material present is a silicon oxynitride. The nitrogen 1s spectrum

for this sample is shown in FIG. 3B, and assignments there indicate the presence of both organic (e.g., C-N) and inorganic nitride (e.g., Si-N) compounds. From the full-range spectrum for this sample (not shown) an elemental quantification finds the line intensities of N:O being about 10:1.

FIGs. 4A and 4B are graphs of the XPS of a sample that was exposed to a nitrogen cluster beam onto an unheated HF-etched surface of silicon. In FIG. 4A, the Si 2p line from silicon in the sample described herein as the nitridation of hydrogen-terminated silicon surfaces. The N 1s line for this sample shows somewhat less organic nitrogen bonding than for the previous sample in FIG. 4B. Some fluorine was also found and is likely a result of less than optimal HF processing.

FIGs. 5A-5C are graphs of the XPS of a sample described herein as deposition of Ga and N that was exposed to nitrogen cluster and gallium beams onto an unheated HF-etched surface of silicon. FIG. 5B showing the Ga 3d spectral line is perhaps the most interesting since it shows that both Ga-O and Ga-N bonds are present, with most Ga in the former compound. From the N 1s line in FIG. 5C, it appears that most of the nitrogen has bonded to the gallium. The ratio of total Ga:N is measured thus to be about 2:1 for this film. Again, a considerable amount of oxygen was present.

FIGs. 6A-6C are graphs of the XPS of a sample described herein as deposition of Ga and N that was exposed to nitrogen cluster and gallium beams onto the surface of sapphire at about 750°C. The Al 2p line of FIG. 6A appears to be entirely Al-O bonds but the Al-N binding energy is similar. The Ga 2p line of FIG. 6B shows mostly Ga-O bonds but some Ga-N is present. The N 1s line of FIG. 6C shows a broader peak than did the previous sample, and likely more contribution from organic nitrogen due to the higher baseline pressure during that particular deposition run. The ratio of total Ga:N is about 1:2 for this film, the reverse of that for the previous film. Again, a considerable amount of oxygen was present.

Although the present invention has been shown and described with respect to several preferred embodiments thereof, various changes, omissions and additions to the form and detail thereof, may be made therein, without departing from the spirit and scope of the invention.

What is claimed is:

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CLAIMS

1   1. A method of forming a silicon nitride film comprising:

2   providing a silicon substrate with a surface;

3   forming a gas cluster ion beam with clusters of nitrogen gas having at least 100

4   atoms, ionized with a single charge on each cluster, and accelerated to no more than

5   100eV per atom; and

6   irradiating said surface with said beam in a vacuum, said beam incident to said

7   surface so as to not substantially penetrate below said surface, in order to form said silicon

8   nitride film.

1   2. The method of claim 1 further comprising processing said silicon nitride film

2   at an elevated temperature including a rapid thermal anneal.

1   3. The method of claim 1, wherein said film substantially consists of Si_3N_{4-x},

2    $x < 0.4$, and no more than 10% silicon-oxygen compounds incorporated, including those

3   with no oxygen and no more than 1% of hydrogen.

1   4. The method of claim 1, wherein said nitrogen gas includes no more than 25%

2   of added hydrogen or helium gas and in such a manner that substantially only the nitrogen

3   gas is incorporated into the gas clusters from which said gas cluster ion beam is formed.

1   5. The method of claim 1 wherein said gas cluster ion beam comprises both

2   clusters of nitrogen and clusters of oxygen, thus forming a film substantially consisting

3   of a silicon-oxygen-nitrogen compound or silicon oxynitride as $Si_3N_{4-x}O_x$ and $x > 0.4$.

1   6. The method of claim 5, wherein said film comprises multiple layers of

2   substantially silicon nitride compound or silicon oxide compound with a silicon oxynitride

3   film layer stacked in any sequence.

1   7. The method of claim 1 further comprising irradiating said surface with a

2   separate oxygen cluster beam, thus forming a film substantially consisting of a silicon-

3   oxygen-nitrogen compound or silicon oxynitride as $Si_3N_{4-x}O_x$ and $x > 0.4$.

1   8. The method of claim 1, wherein said surface is at about room temperature.

1   9. The method of claim 1, wherein said surface is held at an elevated temperature

2   between 200 and 900°C.

1   10. The method of claim 1, wherein said surface is processed in a chamber

2   containing a low pressure below 10^{-3} Torr of nitrogen or nitrogen-containing gas.

1   11. The method of claim 1 further comprising simultaneously irradiating said

2   surface with silicon atoms, ions or silicon-containing compounds or their ions.

1   12. The method of claim 11, wherein said simultaneous irradiation comprises

2   thermal evaporation, electron-beam evaporation, rf-plasma sputtering, ion-beam

3   sputtering, or pulsed laser deposition.

1   13. The method of claim 1, wherein a stencil mask is utilized on, or in close

2   proximity to, said surface.

1   14. The method of claim 1, wherein a rare gas is added to the ionized nitrogen

2   clusters or said beam.

1   15. The method of claim 1, wherein an individual argon-cluster beam is added to

2   that of the nitrogen-cluster beam in a fashion to alternately pulse the argon and nitrogen.

1   16. The method of claim 1, wherein said beam comprises at least one silicon-

2   containing gas compound either as a mixture of nitrogen clusters and clusters containing

3   silicon or as clusters containing within each both nitrogen and the silicon-containing gas

4   compound in such a manner as to cause said beam to react at said surface with said silicon-

5   containing gas compound, thereby forming a silicon nitride film on said surface.

1   17. A method of forming a silicon nitride film comprising:

2   providing a silicon substrate with a surface;

3   forming a gas cluster ion beam with clusters of a nitrogen-containing gas

4   compound, including N_2, NH_3, CN and mixtures of any of these, including at least 100

5   individual molecules, ionized with a single charge on each cluster, and accelerated to no

6   more than 100eV per individual molecule; and

7   irradiating said surface with said beam, said beam incident to said surface so as to

8   not substantially penetrate below said surface, in order to form said silicon nitride film.

1   18.   The method of claim 17, wherein said surface is processed in a chamber

2   containing a low pressure below 10^{-3} Torr of nitrogen or nitrogen-containing gas, with

3   oxygen or oxygen-containing gas, or with hydrogen or hydrogen-containing gas.

1   19.   A method of forming a metal-nitride compound film comprising:

2   providing a substrate which is metal or includes a metal film having a surface;

3   forming a gas cluster ion beam with clusters of nitrogen gas including at least 100

4   atoms, ionized with a single charge on each cluster, and accelerated to no more than

5   100eV per atom; and

6   irradiating said surface with said beam, said beam incident to said surface so as to

7   not substantially penetrate below said surface, in order to form said metal-nitride film.

1   20.   The method of claim 19, wherein said substrate of metal or metal film

2   comprises titanium, tungsten, tantalum, aluminum, indium, gallium or multiple-metal,

3   alloy compounds.

1   21.   The method of claim 19, wherein said metal-nitride film is formed by

2   simultaneous irradiation of said surface with metal atoms, ions or metal-containing

3   compounds or their ions.

1   22.   The method of claim 21, wherein said simultaneous irradiation comprises

2   thermal evaporation, electron-beam evaporation, rf-plasma sputtering, ion-beam sputtering

3   or pulsed-laser deposition.

1   23.   The method of claim 19, wherein said substrate comprises monocrystalline

2   silicon, sapphire, gallium arsenide, gallium aluminum arsenide, aluminum nitride, gallium

3   nitride, indium nitride, gallium aluminum nitride, gallium aluminum indium nitride or thin

4   films of any of these prefabricated onto any other substrate material.

1   24. The method of claim 19, wherein the nitrogen gas has up to 25% of added

2   hydrogen or helium gas such that substantially only the nitrogen gas is incorporated into

3   the gas clusters from which said beam is formed.

1   25. The method of claim 19, wherein a rare gas is added to the ionized nitrogen

2   clusters or said beam.

1   26. The method of claim 19, wherein an individual argon-cluster beam is added

2   to that of the nitrogen-cluster beam in a fashion to alternately pulse the argon and nitrogen.

1   27. The method of claim 19 further comprising irradiating said surface with a

2   separate oxygen cluster beam, thus forming a film substantially consisting of a metal-

3   oxygen-nitrogen compound.

1   28. A system for forming a silicon nitride film comprising:

2   means for forming a gas cluster ion beam with clusters of nitrogen gas having at

3   least 100 atoms, ionized with a single charge on each cluster, and accelerated to no more

4   than 100eV per atom; and

5   means irradiating a surface of a silicon substrate with said beam in a vacuum, said

6   beam incident to said surface so as to not substantially penetrate below said surface, in

7   order to form said silicon nitride film.

1   29. A system for forming a silicon nitride film comprising:

2   means for forming a gas cluster ion beam with clusters of a nitrogen-containing gas

3   compound, including N_2, NH_3, CN and mixtures of any of these, including at least 100

4   individual molecules, ionized with a single charge on each cluster, and accelerated to no

5   more than 100eV per individual molecule; and

6   irradiating a surface of a silicon substrate with said beam, said beam incident to

7   said surface so as to not substantially penetrate below said surface, in order to form said

8   silicon nitride film.

1   30. A system for forming a metal-nitride compound film comprising:

2   means forming a gas cluster ion beam with clusters of nitrogen gas including at

3   least 100 atoms, ionized with a single charge on each cluster, and accelerated to no more

4   than 100eV per atom; and

5   means for irradiating a surface of a substrate which is metal or includes a metal

6   film with said beam, said beam incident to said surface so as to not substantially penetrate

7   below said surface, in order to form said metal-nitride film.

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Nitrogen Sources for Nitride-Semiconductor Film Deposition

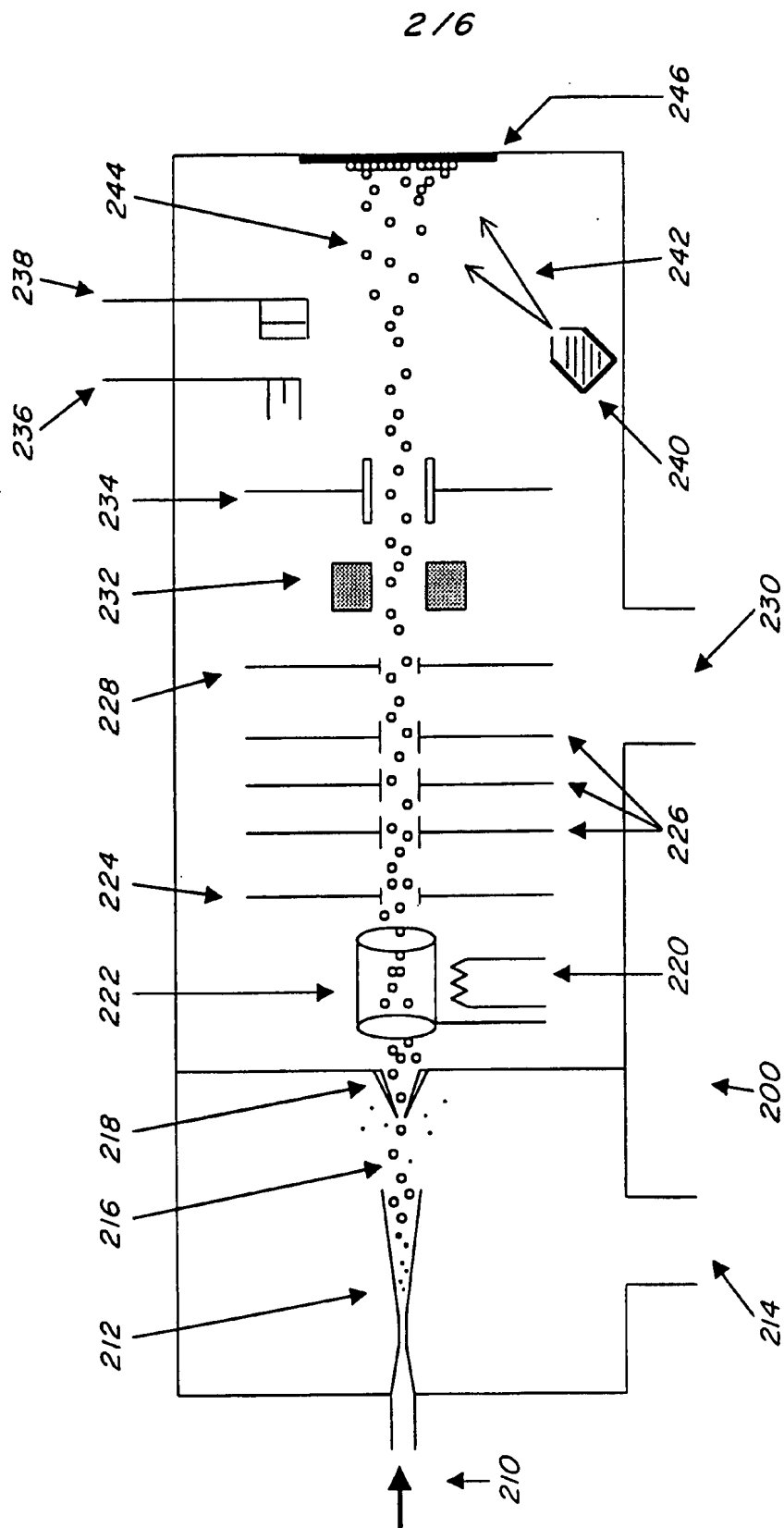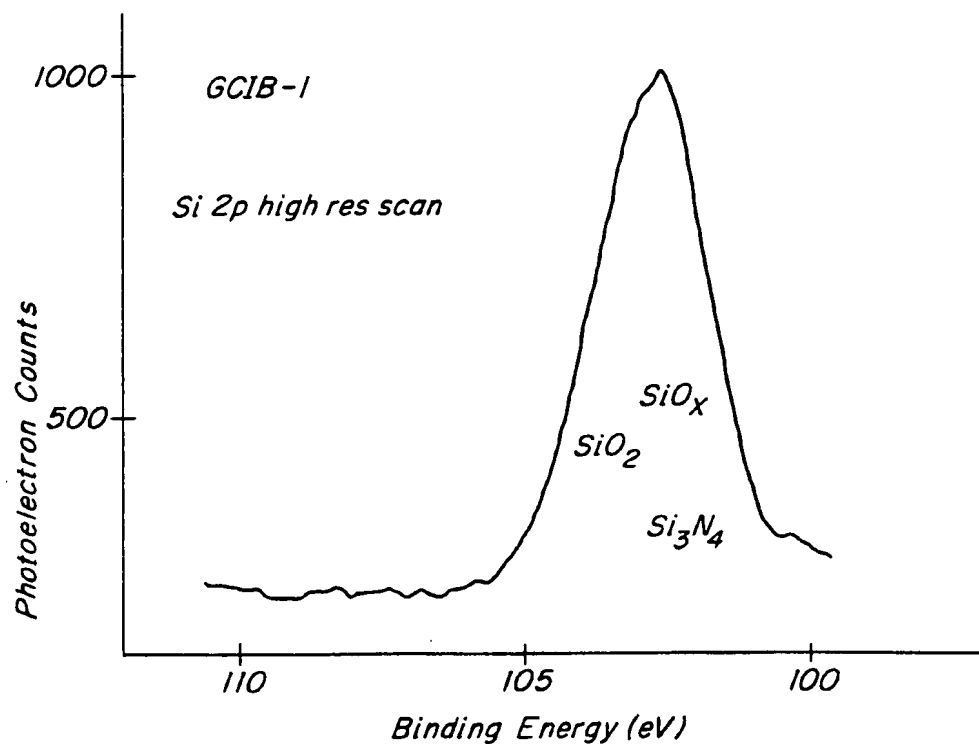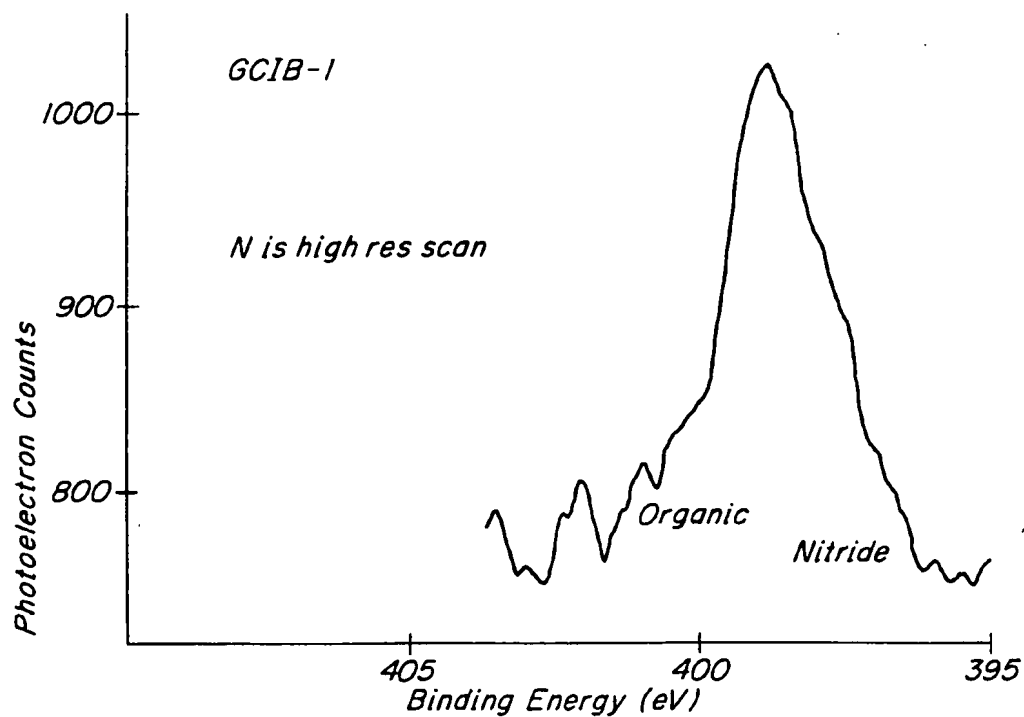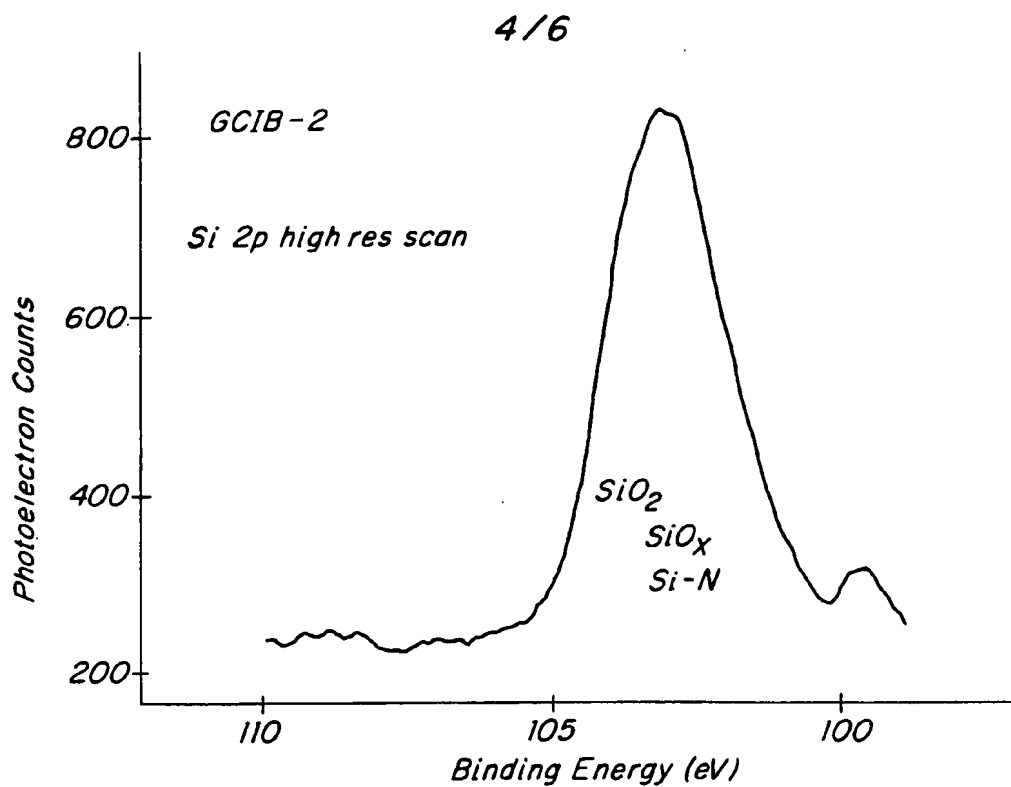| Source	Features	Benefits	Disadvantages
RF-Plasma Nitrogen	High density of radicals and excited states of atomic nitrogen. Pure-nitrogen source gas.	Rapid film growth. Nitridation reactions by multiple routes. Low impurity in films.	Device quality limited by damage to film caused by energetic-radical attack.
ECR Nitrogen	High density of radicals and nitrogen ions. Pure-nitrogen source gas.	Higher reactivity and film growth rates due to presence of nitrogen ions.	Low efficiency. Device quality limited by damage to film by energetic-ion attack.
Ammonia gas-source	No complex equipment or vacuum electronics.	Simplicity of concept and established history of use in CVD industry.	Device quality limited by impurities in gas. Waste gas disposal.
Cluster Ion-Beam Nitrogen (GCIB)	Very low-energy ions with collision-induced reactions. Pure nitrogen gas or optional ammonia.	Potential to be efficient at nitridation without ion damage to film or impurity.	Low deposition rates at present, due to low beam currents. Device film quality not known.

FIG. 1

FIG. 2

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FIG. 3A

FIG. 3B

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FIG. 4A

FIG. 4B

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FIG. 5A

GCIB-3

Si 2s high res scan

Oxide

Si

Photoelectron Counts (y-axis: 400, 500, 600, 700)

Binding Energy (eV) (x-axis: 160, 155, 150)

FIG. 5B

GCIB-3

Ga 3d scan

Oxide

Nitride

Photoelectron Counts (y-axis: 400, 500, 600)

Binding Energy (eV) (x-axis: 25, 20, 15)

FIG. 5C

GCIB-3

N is high res scan

Nitride

Photoelectron Counts (y-axis: 2200, 2400)

Binding Energy (eV) (x-axis: 405, 400, 395)

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GCIB-4

Al 2p low res scan

Al$_2$O$_3$

Photoelectron Counts

Binding Energy (eV)

FIG. 6A

Oxide

GCIB-4
Ga 2p low res scan

Photoelectron Counts

Binding Energy (eV)

FIG. 6B

GCIB-4

N is low res scan

Photoelectron Counts

Binding Energy (eV)

FIG. 6C